July 1948 ET-257

United States Department of Agriculture
Agricultural Research Administration
Bureau of Entomology and Plant Quarantine

A METHOD FOR THE DETERMINATION OF FREON-INSOLUBLE MATTER IN PYRETHRUM EXTRACTS

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Pyrethrum extracts for use in liquefied-gas aerosols vary in their solubility in Freon-12 (dichlorodifluoromethane). This variation depends upon the completeness of the removal of impurities by the manufacturer and the formation of pyrethrin polymerization products. Two methods (1,2) have been published for the determination of the matter insoluble in Freon-12, but under some conditions these methods have given erratic results. Both methods depended upon the formation of deposits on the wall of a container of comparatively great weight but small capacity.

In laboratory studies in this Bureau in 1948, a glass container of greater capacity was used (3), which had been developed to observe liquefied gases, especially at the low temperature (-20° F.) encountered in filling low-pressure aerosol containers. This container was a citrate of magnesia bottle with a capacity of approximately 450 gm. of Freon-12, available at any wholesale drug firm.

The amount of Freon-insoluble material in each of several samples was determined with this container, using concentrations of pyrethrum extract in Freon-12 of from 0.75 to 5 percent. The concentration of 5-percent pyrethrum extract (20 percent pyrethrins) most commonly used for this determination was found to give inconsistent results. More uniform results were given with 0.75- to 2-percent concentrations of pyrethrum extract in Freon-12, but with certain types of extracts the insoluble material failed to adhere to the walls of the container and was subsequently lost when the Freon-12 was released. This insoluble material, unless allowed to stand for several hours, will pass through common filters, so a filter was devised which will retain it when sufficient time is allowed for the suspended material to coagulate.

The assembly and arrangement of integral parts is shown in figure 1. It is essentially the same apparatus as the one described by Fulton and Berlin (3), with the addition of a filter equipped with a 200-mesh stainless steel screen and a lamb's wool plug to retain all of the insoluble material. A Y valve (D) with a 3/8-inch pipe thread is first machined to the exact shape of the glass plug furnished with the citrate of magnesia bottle. The end of the valve is then threaded on a turning lathe to fit the threads of the screen filter unit (A) furnished on oil burner tips. A neoprene washer (C) made from 1/8-inch stock is cut to fit in the groove

of the valve. The center of the filter is then filled with lamb's wool (B) to form a tight fitting plug. This whole unit is thoroughly washed in acetone and chloroform and dried before use. The bottle is next cleaned with a freshly prepared solution of ethyl alcohol and sulfuric acid and rinsed several times with distilled water. Both units are dried in an oven at 105° C. for 1 hour and cooled in a desiccator.

Six grams of the pyrethrum concentrate to be analyzed is weighed into the citrate of magnesia bottle. The most satisfactory method of doing this is to partially fill with the pyrethrum extract a 30-ml. round dropping bottle, having a ground-in glass dropper equipped with a rubber bulb. The pyrethrum extract is then put directly into the citrate of magnesia bottle and the weight determined by difference. The valve is clamped to the neck of the bottle, and the assembled apparatus is evacuated to a residual pressure of 1 inch (25 mm.) of mercury to remove the air and to facilitate filling with Freon-12. A filling device such as described by Fulton et al. (4) is used to add 294 gm. of refrigeration-grade Freon-12. As a safety measure the bottle is wrapped with a heavy cloth before the filling operation. It is then placed in a rack at an angle which will permit the greatest area of glass surface to contact the liquid (fig. 1). After the bottles have been put in the rack a safety glass screen must be placed between them and the operator to give protection during the period while the bottles are being handled and observed.

The bottles are allowed to stand for 10 minutes and are then rotated approximately 45 degrees. This operation is repeated every 10 minutes for 2 hours; then the bottles are allowed to stand overnight. At the end of this time the solution will be clear, in most cases, with all of the insoluble matter adhering to the side of the bottle. The insoluble material from a few commercially prepared extracts has been found to float on the surface of the Freon-12 for several days, later settling to the bottom of the container. This material is retained on the filter, when the Freon-12 is removed from the bottle, by holding the valve down and slowly releasing the liquefied gas. After all this liquefied gas has been released, 200 gm. more of Freon is put into the bottle, and the contents rinsed by shaking the bottle several times. This Freon is then released in the same manner as described above.

The Y valve is then removed, and the filter is taken out with small forceps and placed in a 10-ml. beaker. Five to 7 ml. of chloroform is added and the filter unit allowed to extract while the removal of the residue from the bottle is completed. This operation is performed by slowly adding 15 ml. of chloroform while rotating the bottle, which is then held in a horizontal position and slowly rotated further. The solution is transferred to a weighed 125-ml. Erlenmeyer flask to which several glass beads have been added before weighing. This washing procedure is repeated with three successive 15-ml. portions of chloroform or until no visible deposit remains on the wall of the bottle.

The chloroform from the 10-ml. beaker containing the filter assembly is then transferred to the Erlenmeyer flask. The beaker and filter are

rinsed twice with 5-ml. portions of chloroform, and these portions also transferred to the flask. The chloroform is then removed from this flask by letting it slowly evaporate over a steam bath.

After the chloroform has been entirely removed, the flask is placed in an oven at 105° C. for 1 hour and then transferred to a desiccator and allowed to cool for 2 hours. The flask is weighed, and the Freon-insoluble material calculated as follows:

$$\frac{\text{Weight of residue} \times 100}{\text{Weight of sample}} = \%\ \text{Freon-insoluble material}$$

The results of determinations of the Freon-insoluble material in 2-percent concentrations in four samples of 20-percent pyrethrum extracts are shown in the following tabulation:

Sample No. 1	3.18 percent 3.11
2	1.56 1.53
3	2.66 2.78
4	0.99 1.24

All of these extracts had insoluble material of different appearance.

Literature Cited

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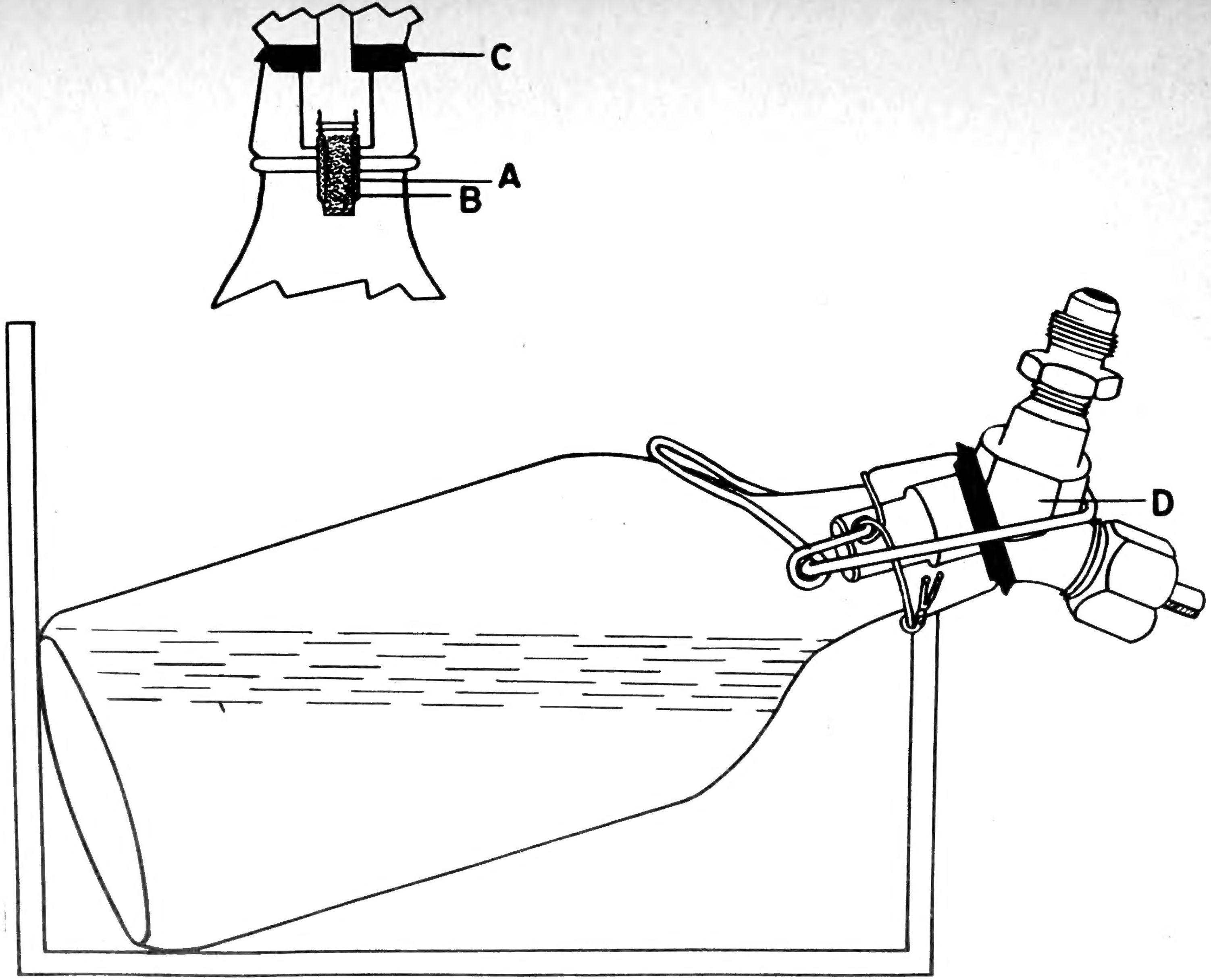

Figure 1.—Apparatus for determination of Freon-insoluble matter in pyrethrum extracts, showing arrangement of integral parts: (A) Filter unit, (B) lamb's wool plug, (C) neoprene washer, (D) Y valve.